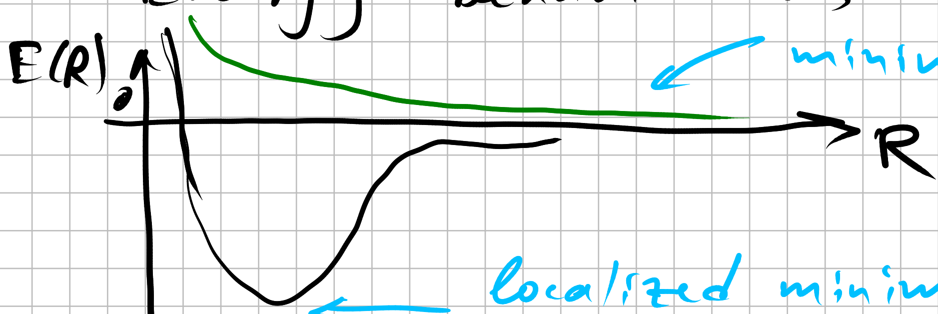
Molecules (at least simple ones)

We saw that there is no analytical solution for He (1 nucleus and 2 electrons), so there is little hope to have solutions for a general molecule (<u>many</u> electrons and at least two nucleus).

So in general we would be concern with a question: can the system bound? i.e. is combined ground state energy <u>lower</u> than constituting parts?

If we somehow can predict the ground level Energy behavior vs R (nucleus separation)

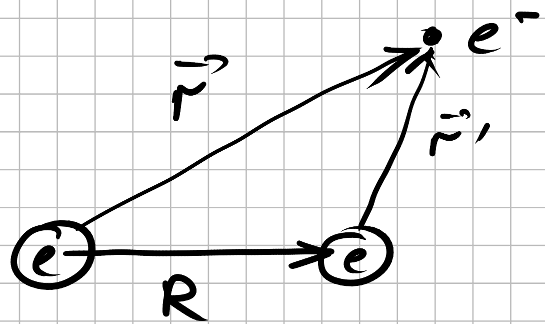


minima at infinity $\Longrightarrow$ no bound state

localized minima $\Longrightarrow$ bound state exist

Hydrogen molecule ion

this is the next "easiest" case



Born-Oppenheimer approximation

Nucleus are heavy $\Rightarrow$ slow so we will disregard their relative motion with respect to the center of mass.

$$\hat{H} = \frac{p^2}{2M_e} - \frac{e^2}{r} - \frac{e^2}{r'} + \frac{e^2}{R}$$

nucleus repulsion

R is constant in our model!

for any ψ

$$\left\langle \frac{e^2}{R} \right\rangle = \frac{e^2}{R} = \frac{e^2}{a_0}\frac{a_0}{R} = -\frac{2a_0}{R}\cdot E_g(z=1)$$

Hydrogen ground energy

As usual, the art is in chosing good anzatz ψ.

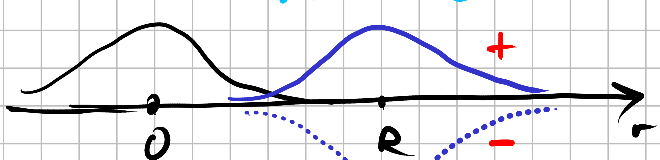
We will use

Hydrogen ground level eigen state

$$\psi = C\left(\psi_{10}(r) \pm \psi_{10}(r')\right), \qquad \vec{r}\,' = \vec{r} - \vec{R}$$

n l

right now it is unclear which + or − is better. But if we think that two nuclei repel each other $\Rightarrow$ we need electron in between, so '+' is more promising



ψ in the form of $\left(\psi_{10}(r) + \psi_{10}(r')\right)$ is what quantum chemist call a linear combination of atomic orbitals (LCAO).

Our 1st task to normilize ψ

$$\langle\psi|\psi\rangle = c^2 \Big(\overbrace{\langle \psi_{10}(r) | \psi_{10}(r)\rangle}^{=1} + \overbrace{\langle \psi_{10}(r') | \psi_{10}(r')\rangle}^{=1} + \pm 2 \langle \psi_{10}(r) | \psi_{10}(r')\rangle \Big)$$

$$= c^2 2 \big(1 \pm \underbrace{\langle \psi_{10}(r) | \psi_{10}(r')\rangle}_{\text{overlap integral which we label } I} \big)$$

Recall $\psi_{10}(r) = \frac{1}{\sqrt{\pi a^3}} e^{-r/a}$

Calculation of I is tidious (see Ch.8 Griffiths)

$$\boxed{\begin{aligned} I &= e^{-R/a}\left[1 + \left(\frac{R}{a}\right) + \frac{1}{3}\left(\frac{R}{a}\right)^2\right] \\ c^2 &= \frac{1}{2(1 \pm I)} \end{aligned}}$$

Next we need the expectation value of truncated $\hat{H}_T$ (no nucleus repulsion) $\frac{p^2}{2m} - \frac{e^2}{r} - \frac{e^2}{r'}$

Observe that

$$\hat{H}_T |\psi_{10}(r)\rangle = \Big(\underbrace{\frac{p^2}{2m} - \frac{e^2}{r}}_{\hat{H} \text{ of } H_{\text{hydrogen}}} - \frac{e^2}{r'} \Big) |\psi_{10}(r)\rangle =$$

$$= \underbrace{E_g(z=1)}_{\text{ground energy of Hydrogen}} |\psi_{10}(r)\rangle - \frac{e^2}{r'} |\psi_{10}(r)\rangle$$

prime ↑ no prime

Similarly

$$\hat{H}_T |\psi_{10}(r')\rangle = E_g(z=1) |\psi_{10}(r')\rangle - \frac{e^2}{r} |\psi_{10}(r')\rangle$$

$$\langle \psi | H_T | \psi \rangle = \langle \psi | H_T | \underbrace{C(\psi_{10}(r) \pm \psi_{10}(r'))}_{\psi} \rangle =$$

$$= E_g(z=1) - c^2 e^2 \Big(\langle \psi_{10}(r) \pm \psi_{10}(r') | \Big(\frac{1}{r'} |\psi_{10}(r)\rangle \pm \frac{1}{r} |\psi_{10}(r')\rangle \Big) \Big)$$

$$= E_g(z=1) - c^2 e^2 \Big[\langle \psi_{10}(r) | \frac{1}{r'} | \psi_{10}(r) \rangle \pm \langle \psi_{10}(r) | \frac{1}{r} | \psi_{10}(r') \rangle$$

" ← variable relabel → "

$$\langle \psi_{10}(r') | \frac{1}{r} | \psi_{10}(r') \rangle \pm \langle \psi_{10}(r') | \frac{1}{r'} | \psi_{10}(r) \rangle \Big]$$

$\leftarrow E_g(z=1)$

$$\langle H_T \rangle = E_g(z=1) - \frac{2C^2 z e^2}{2a}\Big[\underbrace{a\langle \psi_{10}(r)|\tfrac{1}{r'}|\psi_{10}(r)\rangle}_{D\text{ - direct integral}} \pm \underbrace{a\langle \psi_{10}(r)|\tfrac{1}{r}|\psi_{10}(r')\rangle}_{X\text{ - exchange integral}}\Big]$$

$$\boxed{\begin{aligned} D &= \frac{a}{R} - \left(1+\frac{a}{R}\right)e^{-2R/a} \\ X &= \left(1+\frac{R}{a}\right)e^{-R/a} \end{aligned}}$$

$$\boxed{\langle H \rangle = \langle H_T \rangle - \underbrace{\frac{2a}{R}E_g(z=1)}_{\text{nuclear repulsion}} = \left[\left(1 + 2\,\frac{D \pm X}{1 \pm I}\right) - \underbrace{\frac{2a}{R}}\right]E_g(z=1)}$$

notice that we can introduce unitless parameter $\lambda = \frac{R}{a}$ and search for minimum

λ_{min} for $(+)$ case $\frac{R}{a} = 2.4 \implies R = 1.3\,\text{Å}$

$$\langle H \rangle - E_g(z=1) = 1.8\ \text{eV}$$

https://quantummechanics.ucsd.edu/ph130a/130_notes/node398.html